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PATENT SPECIFICATION

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(19)

(54) IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF SHAPED CARBON BODIES

(71) We, SIGRI ELEKTROGRAPHIT GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG, a German Company, of 5 8901 Meitingen bei Augsburg, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a process for the production of carbon bodies from mixtures of carbon-containing solids and hardenable binders.

15 Masses for shaping to produce shaped carbon bodies are generally produced from mixtures of carbon-containing solids and binders. It is a feature of such masses that they generally consist of a mixture of solid and liquid phases. The solid phase can comprise petroleum coke, pitch coke, carbon black or graphite and is inert on carbonisation, having a content of fixed carbon of almost 100%. The liquid phase owes its presence to the binder used which can consist of coal tar pitch or synthetic resins and which contains considerable quantities of volatile carbon compounds. To achieve almost 100% content of fixed carbon throughout the shaped carbon bodies, carbonisation of the binders must be effected. The consequent splitting off of the volatile compounds during the carbonisation treatment, results in tensile stresses being set up at the phase boundaries. These stresses initiate formation of cracks 30 which are detrimental to the quality of the shaped bodies and may result in complete destruction of the bodies. In order to reduce the magnitude of these harmful, stresses, attempts have been made to use pitches and resins with low contents of volatile substances, as binders. However, such binders have insufficient pliability and wettability, so

that shaped masses for carbonisation could not be produced.

In order to overcome this problem, it has been proposed in German Patent Specification No. 1,113, 214, to produce a single phase carbonisable shaped mass from which carbon and graphite bodies of a low gas permeability can be produced. The single phase mass is produced by suspending in water cellulose ground to extremely fine form, dehydrating the suspension obtained to produce a shaped mass and carbonising or graphitising the shaped mass by slow heating with exclusion of air. Owing to the two-stage heating procedure involved, it is not possible to produce shaped bodies of accurate dimensions by this method. Dehydration of the suspension results in shrinkage of about 50% occurring and the subsequent carbonisation results in shrinkage by about 32%.

According to one aspect of this invention, there is provided a process for the production of a shaped carbon body, which comprises shaping a mixture of a powdered or chip-form carbon-containing solids component which can be transformed into carbon without passing through a liquid or plastic phase, by heating in an inert atmosphere and a carbon-containing liquid synthetic resin which forms a solid infusible mass under the action of heat or catalysts and subjecting the shaped mass obtained to a carbonisation heat treatment in an inert atmosphere, the solids component and liquid synthetic resin both undergoing weight losses of from 40 to 60% during the carbonisation heat treatment.

According to a second aspect of this invention, there is provided a composition suitable for use in the process of this invention for the production of a shaped carbon body, comprising a powdered or chip-form carbon-containing solids component which

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can be transformed into carbon without passing through a liquid or plastic phase, by heating in an inert atmosphere and a carbon-containing liquid synthetic resin which forms a solid infusible mass under the action of heat or catalyst, the resin and the solids component both undergoing weight losses of from 40 to 60% when subjected to a carbonisation heat treatment.

This invention is based on the discovery that, the formation of quality-reducing cracks during the carbonisation of a two phase shaped mass can be avoided if the solids and liquid synthetic resin used as binder in the shaped masses both undergo shrinkage to a similar extent during carbonisation of the resin. The solids and resin will generally both shrink by the same amount in all directions. Shaped bodies produced according to the invention are free from internal stresses and present a uniform structure similar to that of glass-like carbon. They remain substantially unaffected by change in temperature. Since the solids and resins will generally shrink by the same amount in all directions the process is reproducible and shaped bodies of any kind and also of relatively large dimensions can be produced to accurate dimensions.

The solids and resins used will preferably undergo the same percentage loss in weight. Solids which will undergo shrinkage during carbonisation of the binders will generally undergo carbonisation themselves, but will not yield volatile cleavage products to the same extent as the resins, if they yield volatile cleavage products at all. Such solids will generally comprise cellulose, such as sawdust, and/or ground hardened synthetic resins.

Preferred resins for use in the process according to the invention are hardenable synthetic resins, such as phenol formaldehyde resins, furan resins or mixtures of these resins.

Carbon bodies of lower fluid permeability can be obtained, if according to a preferred embodiment of the invention, the shaped masses are coated before the carbonisation stage with a film consisting of hardenable synthetic resin which, when carbonised forms a vitreous carbon layer which resin undergoes weight loss of from 40 to 60% during the carbonisation heat treatment. The use of phenol formaldehyde resins, furan resins or a mixture of these resins if preferred. The thickness of the synthetic resin film is preferably less than 1 mm.

Hardening, cross-linking and carbonising of the film coating yields a carbon coating of a glass-like appearance.

Since the films are formed of the same types of material as the binder resin, they show the same shrinkage behaviour as the shaped bodies during hardening and carbonisation, so that stresses in the boundary region between synthetic resin film and basic body are avoided during the heating process.

When carrying out the process according to the invention, the solids material in powder or chip form, generally after a suitable drying treatment in the case of cellulose-containing materials is liquid synthetic resin, and formed into the desired shape. The two phase mixture of solids and resin binder will generally be of such a consistency as to permit the spreading thereof on a support e.g. by trowelling. Alternatively, the required shaped mass for hardening and carbonisation can be formed by pressing or vibrating.

The resin binder is thereafter hardened by heating the shaped mass to 100 to 200°C and the shaped masses are then carbonised by further heating in an inert atmosphere to 800 to 1000°C. The rise in temperature between 350 and 600°C will generally be at a rate of from 3 to 4 C/h. The linear shrinkage during the carbonisation is about 22%. If desired, the carbonised bodies can be graphitised by further heating to temperatures of at least 2500°C, the shaped bodies then shrinking by 6 to 7%. When hardened resins are to be used as solids material, a hardenable synthetic resin, for example phenol formaldehyde resin or a furan resin is heated in a mould to a temperature of about 200°C and the solid resin mass thereby formed is ground after cooling to room temperature.

In order to produce shaped carbon bodies of increased fluid impermeability as mentioned hereinabove, synthetic resins, which can contain hardening catalysts, are sprayed or brushed on to carbon-containing shaped masses which have been hardened by heating usually at a temperature of from 100 to 200°C. The synthetic resin film is then hardened by a further heating of the masses usually to a temperature of from 100 to 200°C and is then carbonised together with the basic shaped carbon mass as aforesaid possibly followed by graphitisation. A layer of glass-like carbon is formed from the synthetic resin layer. The carbon layer has a very low permeability and adheres to the basic material.

The carbon or graphite bodies produced by the process according to the invention are particularly suitable for use as refractory linings, linings of electrolysis cells and furnace insulations. These shaped bodies which are coated with synthetic resin films and thereafter carbonised to render them practically impervious to liquids and gases have the further property that the glass-like surface layer, when produced, has a very high resistance to wear and is very stable with respect to oxidising substances. Such coated carbon bodies are thus particularly suitable for use as electric contacts, electrodes, linings of chemical apparatus and metallurgical vessels, and as

bearings and bearing rings, when suitably shaped for the particular use.

The following examples illustrate the present invention:

5 **Example 1**

To 800 g of sawdust having a grain size of 500 to 1000 μm mixed with 330 g of furfuryl alcohol were added 2% of methylcellulose and 3% of p - toluosulphonic acid.

10 The mixture obtained was of smooth consistency and was applied by trowelling to a hemispherical mould made of steel, and then hardened by heating in a drying chamber at 150°C. After removing the metal mould, the shaped mass obtained was heated in a round down-draught kiln. The rise in temperature between 400 and 700°C was about 3.5°C/h, and the maximum temperature achieved was 1050°C.

20 The spherical shell-like bodies obtained shrank tangentially by about 20% and radially by about 24% during the carbonisation. The loss in weight during the carbonisation was 48.5%. The carbonised body possessed the following physical properties:

bulk density:	1.07 g/cc
true density:	1.55 g/cc
bending strength:	105 kp/cm ²
elasticity modulus:	700,000 kp/cm ²
coefficient of thermal expansion:	(20—1000°C) $2.9 \times 10^{-6}/^\circ\text{C}$
thermal conductivity:	0.65 Kcal/mh°C

Example 2

About 500 g of phenol formaldehyde resin having a viscosity of about 2800 cp were hardened in shallow moulds at a temperature of 190°C and then ground in a ball mill. 2500 g of ground resin were then mixed with 1500 g. of furfuryl alcohol, 1000 g. of phenol formaldehyde resin and 100 g. of oxalic acid and then compressed into the form of a cylindrical body. Hardening and carbonisation were effected by the heating procedure set out in Example 1.

45 The carbonised cylinder was then graphitised in a resistance furnace at a temperature of about 2800°C. The graphitised body possessed the following physical properties:

bulk density:	1.35 g/cc
true density:	1.56 g/cc
bending strength:	200 kp/cm ²
coefficient of thermal expansion:	(20—1000°C) $3.1 \times 10^{-6}/^\circ\text{C}$

Example 3

55 40 g of sawdust were dried at 120°C and mixed with 200 g of furfuryl alcohol and the mixture was compressed into the shape of crucibles. The crucible masses were heated in an electric furnace to 180°C, cooled to room temperature and then coated with a

layer of furfuryl alcohol. The crucibles were then once again subjected to a hardening treatment at 180°C after which they were heated up to 1000°C in a round down-draught kiln.

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The carbonised crucibles obtained had a surface layer of glass-like carbon in a thickness of 0.5 mm. The surface layer was firmly anchored to the base material and remained free from cracks after the crucibles had been heated to 1000°C and quenched in water several times. A mixture (1:1) of 60% nitric acid and 30% hydrochloric acid was maintained in some of the crucibles for 24 hours at about 30°C. The loss in weight of the crucibles was less than 0.01%.

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Example 4

Plates having a thickness of 30 mm were pressed from a mixture with a composition set out in Example 3. After carrying out the first hardening procedure of Example 3 these plates were spray coated with a layer about 1 mm thick of phenol formaldehyde resin. The plate was then heated to harden the film coating and carbonised by the procedures of Example 3.

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The thickness of the glass-like carbon film coating obtained after the heating stages was about 0.6 mm and the permeability of the film rating to air was less than $10^{-6} \text{ cm}^3/\text{sec.}$

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WHAT WE CLAIM IS:—

1. A process for the production of a shaped carbon body, which comprises shaping a mixture of a powdered or chip-form carbon-containing solids component which can be transformed into carbon without passing through a liquid or plastic phase, by heating in an inert atmosphere and a carbon-containing liquid synthetic resin which forms a solid infusible mass under the action of heat or catalysts and subjecting the shaped mass obtained to a carbonisation heat treatment in an inert atmosphere, the solids component and liquid synthetic resin both undergoing weight losses of from 40 to 60% during the carbonization heat treatment.

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2. A process as claimed in Claim 1, in which the solids component and liquid synthetic resin undergo the same loss in weight during the carbonisation heat treatment.

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3. A process as claimed in Claim 1 or 2, in which the solids component comprises cellulose.

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4. A process as claimed in Claim 3, in which the solids component comprises sawdust.

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5. A process as claimed in any one of the preceding claims, in which the solids component comprises a group hardened synthetic resin.

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6. A process as claimed in Claim 5, in which the hardened resin is a phenol-formaldehyde resin or a furan resin.

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7. A process as claimed in any one of the preceding claims, in which the liquid synthetic resin comprises a phenol-formaldehyde resin or a furan resin.

5 8. A process as claimed in any one of the preceding claims, in which said mixture has a consistency such as to allow it to be spread on to a support to obtain said shaped mass.

10 9. A process as claimed in any one of the preceding claims in which the shaped mass is hardened at a temperature of from 100 to 200°C. and is carbonised by heating to a temperature of from 800 to 1000°C., the rise in temperature of the shaped mass in the temperature range from 350 to 600°C. being from 3 to 4°C/hour.

15 10. A process as claimed in any one of the preceding claims in which, prior to said carbonisation heat treatment, but subsequent to hardening of the shaped mass, the shaped mass is coated with a film of hardenable synthetic resin which is then hardened, the synthetic resin used to coat the shaped mass being of such a type that it forms a vitreous carbon layer when carbonised and undergoes weight loss of from 40 to 60% during the carbonisation heat treatment.

20 11. A process as claimed in Claim 10, in which the hardenable synthetic resin used to coat the shaped mass comprises a phenol-formaldehyde resin or a furan resin.

25 12. A process as claimed in any one of Claims 10 or 11, in which the coated film has a thickness of not more than 1 mm.

30 13. A process as claimed in any one of the preceding claims, in which the shaped carbon body is graphitised.

35 14. A process for the production of a shaped carbon body, substantially as described in either of the foregoing Examples 1 and 2.

40 15. A process for the production of a shaped carbon body, substantially as described in either of the foregoing Examples 3 and 4.

45 16. A shaped carbon body whenever produced by the process claimed in any one of the preceding claims.

17. A composition suitable for use in the process for the production of a shaped carbon body as claimed in Claim 1, comprising a powdered or chip-form carbon-containing solids component which can be transformed into carbon without passing through a liquid or plastic phase, by heating in an inert atmosphere and a carbon-containing liquid synthetic resin which forms a solid infusible mass under the action of heat or catalyst, the resin and the solids component both undergoing weight losses of from 40 to 60% when subjected to a carbonisation heat treatment.

50 18. A composition as claimed in Claim 17, in which both the resin and the solids components undergo the same weight loss when subjected to a carbonisation heat treatment.

55 19. A composition as claimed in Claim 17 or 18, in which the solids component comprises cellulose.

60 20. A composition as claimed in Claim 19, in which the solids component comprises sawdust.

65 21. A composition as claimed in any one of Claims 17 to 20, in which the solids component comprises a ground hardened synthetic resin.

70 22. A composition as claimed in Claim 21, in which the hardened resin is a phenol-aldehyde resin or a furan resin.

75 23. A composition as claimed in any one of Claims 17 to 22, in which the liquid synthetic resin comprises a phenol-formaldehyde resin or a furan resin.

80 24. A composition as claimed in Claim 17, substantially as described in either of the foregoing Examples 1 and 2.

85 25. A composition as claimed in Claim 17, substantially as described in the foregoing Example 3.

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